STUDIES IN THE POLYMERISATION OF VINYL ACETATE.

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BY

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D E D I C A T I O N

Dedicated to my family for their
love at all times.

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ABSTRACT

The emulsion polymerisation of vinyl acetate has been studied at 40^0C +/- 1 using benzoyl peroxide and ferrous iron as the initiator system. Three different emulsifying agents are used. The effect of emulsifying agent, its concentration and the time of polymerisation on the emulsion properties, the polymer yield and molecular weight have been investigated.

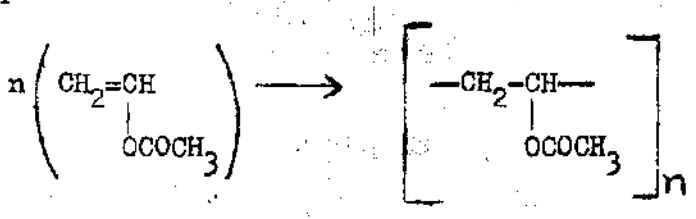
The results show that the generalised theory of emulsion polymerisation applies to a limited extent to this system. The rate of polymerisation is constant between 0-80 percent polymerisation. The molecular weight decreases with time of polymerisation. This has been attributed to increasing rate of initiation with time.

The effect of molecular weight on the tensile properties of the polymer film has been studied. The results show that polymer samples prepared with varying emulsifier concentration have narrower molecular weight distribution when compared to samples obtained at varying time of polymerisation and constant emulsifier concentration.

Chapter 1

1.0 General Introduction

The polymerisation of vinyl acetate can be represented by the chemical equation



vinyl acetate polyvinyl acetate

where n is the number of repeating units.

The monomer (vinyl acetate) is a liquid at ambient temperatures. The properties of interest are shown below.

Table 1

Some Physical Properties of Vinyl acetate

Boiling point	-	72.7°C
Freezing point	-	-92.8°C
Specific gravity at 20°C	-	0.9338
Refractive Index	-	1.3940
Solubility in water at 20°C	-	2.5 percent
Specific heat cal/°C at 20°C	-	0.47

Vinyl acetate shows no known health hazards[1] except that exposure to high concentration of vapour from its polymerisation can be dangerous. This is due to harmful effects of acetaldehyde that

is given off in appreciable amounts. Vinyl acetate is relatively stable at ordinary temperatures but additional stability against polymerisation is achieved by addition of inhibitors such as copper salts, amines or hydroquinones. These inhibitors are added in small amounts but must be removed before polymerisation to get reproduceable results.

1.1 Properties of Polyvinyl Acetate

Polyvinyl acetate is a thermoplastic odorless, tasteless, nontoxic, essentially clear and colourless resin. It has a noncrystalline and relatively branched structure[2]. This is due to the bulky acetate groups on the chain. Most commercial grades have broad molecular weight distribution and for this reason melting or softening is usually over a wide range of temperature. The various grades are known to have good heat stability below 100°C. Slight colouration occurs at 150°C and decomposition is usually between 200-250°C[3]. The softening point for most grades is around 50°C. The polymer becomes brittle at around 10-15°C.

The difference in physical properties of the polymer is due mainly to differences in molecular weight and its distribution. The polymer is graded by the viscosity number (V-number) which is the viscosity in centipoises of a molar solution of polymer in benzene.

The low molecular weight polymers are soft at room temperature whereas the high molecular weight polymers are hard and tough.

The highly polar acetate groups on the polymer gives the polymer excellent adhesion to many surfaces. Some properties of some commercial grades of vinyl acetate (Gelva resins of Shawnigan resin Corporation) which depend on its molecular weight are given below[4].

Table 2

Some Characteristics of Gelva Resins

Grade	Viscosity CP	Molecular weight average	Softening point °C	Maximum tensile strength kg cm^{-2}
V 1.5	1.4-1.70	11,000	65	Too brittle
V.7	6-8	45,000	106	4,100
V.60	54-66	300,000	196	6,500
V.100	90-110	500,000	230	7,200

1.2 Application of Polyvinyl Acetate

Polyvinyl acetate has been available since the 1930's. Production was small until 1940's when polyvinyl acetate emulsions were introduced[5]. The volume consumed has grown from negligible in 1940 to several million pounds as at present.

The low cost of the monomer has made the polymer the principal vinyl polymer of commerce. The adhesive industry is currently the most important outlet for polyvinyl acetate.

1.2.1 Surface Coating Industry

The surface coating is one of the principal uses of the resin. It is almost applied in the emulsion form. As early as the middle

1930's Mowilith series[4] of polyvinyl alcohol based polyvinyl acetate emulsions were used in Germany for formulation of emulsion paints. These early paints were used for exterior masonry and later for interior walls. Of recent vinyl acetate emulsions are used in the formulation of gloss and texture interior paints, exterior wood paints, and industrial primers and finishes.

1.2.2 Paper Industry

The major use of the resin emulsions in this industry is that of coating. The original materials used were casein and starches but in view of their poor wet-rub resistance and liability to bacterial and fungal attack they have been replaced in part by synthetic resin emulsions of which polyvinyl acetate is the most economical. The high tensile strenth possible with polyvinyl acetate has made it useful in adhesive tape backings and book binding materials. Apart from coating polyvinyl acetate can also be used in 'beater' additions during paper manufacture to improve the quality of the paper.

1.2.3. Textile Industry

The polymer is mostly applied in the emulsion form for finishes that impart strength to woven fabrics especially cotton. It can also be used as binders for non woven fabrics. The resin emulsion is also suitable on blends. Partially hydrolysed polyvinyl acetate is used instead of starch for sizing of fabrics. This is because it is easily removed after sizing. There is no colour development as is possible when desizing fabrics sized with starch.

1.2.4. Building Industry

The resin can be used as surface coatings and adhesive for special materials of construction. It can also be used as binder for decorative facings and sealer for porous surfaces in preparation for further treatment. The polymer is used as cement additive to avoid the unpleasant 'hard' characteristics of cement floors and their dustiness. Correct formulation can give balanced properties of sound absorption together with thermal and electrical insulation.

1.2.5. General Adhesive Industry

Polyvinyl acetate and its copolymers are capable of producing adhesives of an almost universal character. Adhesives from emulsions with polyvinyl alcohol stabiliser have special utility as wood adhesives.

1.2.6. Food Industry

The polymer is harmless[1] and therefore suitable for direct contact with food. It is used for coating of various containers for foodstuff to prevent attack by micro-organisms. This allows food to be stored in fresh condition for months. The polymer is also used as a chewing gum base.

1.2.7. Miscellaneous Application

Other uses of the polymer include use in printing inks, coating for stencil screeens and sixing of glass fibres. Surgical and medical applications are known e.g. alcoholic solutions are used as a

replacement for colloidion in dressings. It has also been suggested as a blood plasma substitute.

1.3. Polymerisation of Vinyl Monomers

The process by which vinyl monomers are converted to polymers of high molecular weight exhibit characteristics of typical chain reactions. The process occurs in three stages viz initiation, propagation and termination. The propagation and termination processes are extremely fast taking only a small fraction of a second. Depending on the type of initiator used the polymerisation is classified into (a) Free radical polymerisation (b) Cationic polymerisation and (c) anionic polyerisation.

1.3.1. Free Radical Polymerisation

This is the most common and important type of addition polymerisation of vinyl monomers. The free radicals or chain carriers are obtained by the thermal or photochemical decomposition of compounds such as organic perioxides, azo and diazo compounds e.g. benzoyl peroxide and azobis isobutyronitrile. The initiation reaction can be represented as shown

$$X_2 \longrightarrow 2\ X^{\bullet}$$

$$X^{\bullet} + CH_2 = CRR^1 \longrightarrow XCH_2 - CRR^1 .- \text{ etc.}$$

where X_2 is the initiator.

At each addition one electron of the double bond pairs with that of the free radical and the second electron of the double bond regenerates a free radical which repeats the process. The chain is propagated by addition of a large number of monomer molecules. Termination of growing chains can occur in two ways (1) two growing chains may combine. This is termination by combination.

$$X^{\bullet}\left[CH_2.CRR^1\right]_m + X^{\bullet}\left[CH_2CRR^1\right]_n \longrightarrow X\left[CH_2.CRR^1\right]_{m+n}X$$

(2) hydrogen atom transfer from one growing chain to the other. This is termination by disproportionation.

$$\sim CH_2.CRR^{1}\bullet + \bullet RR^1C.CH_2\sim$$

$$\longrightarrow \sim CH_2.CH\,RR^1 + RR^1C = CH\sim$$

1.3.2. Redox Polymerisation

The rate of radical production at low temperatures can be increased if the decomposition of peroxide type catalysts used in free radical polymerisation is allowed to occur in the presence of a reducing agent such as ferrous ions. Such a system is called a redox system. It allows for polymerisation at very low temperatures, lower than the decomposition temperature of the single initiator.

e.g. $(C_6H_5CO)_2O_2 + Fe^{++} \longrightarrow C_6H_5COO + C_6H_5COO^- + Fe^{+++}$

benzoyl peroxide.

1.3.3. Polymerisation Processes

Free radical addition polymerisation can be carried out in bulk, solution, suspension and emulsion.

(a) Bulk Polymerisation

In this type of process the initiator is added to the undiluted monomer. When free radicals are generated the reaction proceeds at a very fast rate. The polymer formed will dissolve in its monomer. This makes the medium very viscous, heat transfer is not easy and there may be explosion due to excessive heat given off. The polymer from this process is usually very pure but the molecular weight is usually very low and the distribution wide. Separation of the unreacted monomer from the polymer may also be a problem.

(b) Solution Polymerisation

This is when the polymerisation is carried out in a solvent suitable for the monomer, and initiator. The polymer may remain in solution or separate out. If the polymer dissolves in the solvent increasing viscosity of the medium may cause mechanical difficulties and the polymer must be separated by evaporation of solvent or addition of a precipitant. If the polymer separates out removal of adsorbed solvent may be difficult. The molecular weight may be reduced by chain transfer to solvent. Heat transfer is effected by refluxing the solvent.

(c) Suspension Polymerisation

The monomer is suspended in an aqueous phase. The monomer is dispersed in water by agitation and addition of suspension stabilisers. The stabiliser prevents monomer droplets and polymer globules adhering to each other. Polymerisation is effected in each globule and a spherical pearl of high molecular weight is obtained. Heat removal is easy because of the aqueous suspending medium. The disadvantages are: (1) Contamination of polymer with stabiliser.
(2) Loss of monomer due to slight polymerisation in the aqueous phase.

The rate of polymerisation of the monomer and the molecular weight of the polymer product compare favourably with those obtained by bulk polymerisation.

(d) Emulsion Polymerisation

Emulsion polymerisation is a major technique for the polymerisation of vinyl monomers. The suitability of the emulsion for direct application e.g. coatings and finishes and the high rate and high molecular weights possible are some of the major advantages of the method. Other advantages include

(1) the cheapness and non-flammable character of the dispersing medium
(2) the ease of heat control by dispersing medium
(3) and the ease with which products can be pigmented and compounded with addition of good dispersing agent.

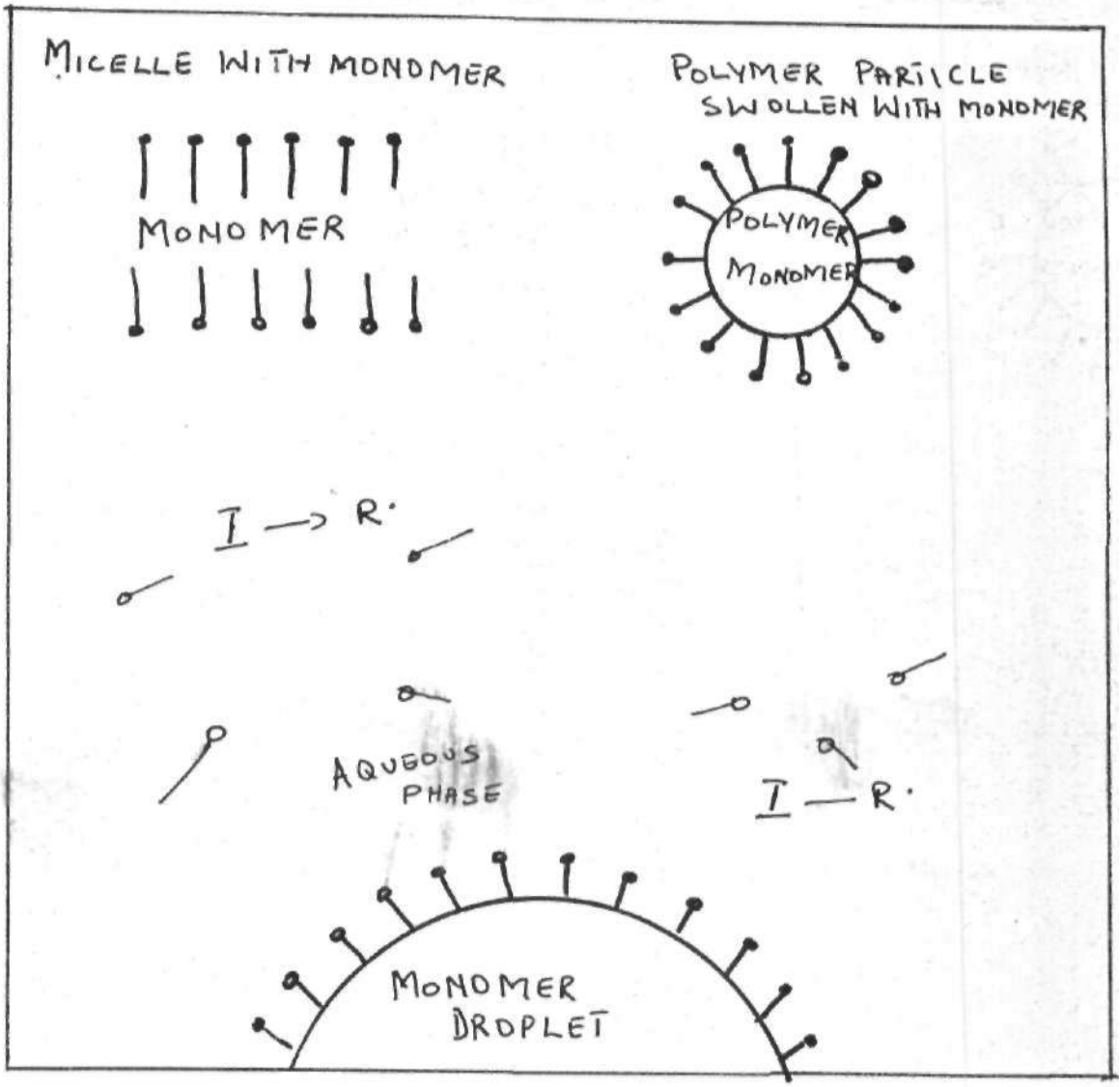


FIG I. SIMPLIFIED REPRESENTATION OF AN EMULSION POLYMERISATION SYSTEM.

o— — EMULSIFIER MOLECULE

I — INITIATOR

R· — INITIATING RADICAL.

This technique is the only one used in the present study and a review of the theory of the process is therefore necessary.

1.3.4. Theory of Emulsion Polymerisation

The currently accepted theory of emulsion polymerisation is due to the work of Harkins[6,7,8], McBain[9], Haward[10], Smith and Ewart[11,12] and their collaborators. The simplified representation of an emulsion polymerisation system is shown in Fig. I.

When the emulsifier e.g. soap is dissolved in water in the right proportions virtually all the soap is present in the form of micelles or oriented aggregates of soap molecules. There is a dynamic equilibrium between the emulsifier in solution and that in the micelles. The micelles are rod like in shape as shown by light scattering measurements[13]. Each micelle consists of 50 to 100 emulsifier molecules and is 1,000 to 3,000Å (0.1-0.3) in length with diameters that are approximately twice the length of an emulsifier molecule. The hydrocarbon and hydrophobic ends of the emulsifier molecules point toward the interior of the micelle while the ionic and hydrophillic ends outward toward the water. The number and size of the micelles depend on the ratio of emulsifier to monomer in the system.

When the liquid monomer is added a very small fraction may go into solution especially for the slightly water soluble monomers.

A larger but still a small fraction enters the interior hydrocarbon part of the micelles. This is evidenced by X-ray and light scattering measurements which show that micelles increase in size as the monomer is added[13]. The largest portion of the monomer is dispersed as monomer droplets whose size depends on the intensity of agitation. The droplets are stabilised by emulsifier molecules adsorbed on their surfaces. If the initiator is water soluble it dissolves in the aqueous phase where the initiating radicals are produced. The radicals diffuse into the interior of the micelles where they initiate polymerisation of the solubilised monomer. The high monomer concentration in the micelles and the high surface to volume ratio of the micelles favour the rapid polymerisation.

The micelles grow in size as polymerisation progresses by addition of monomer from the aqueous phase. When this is exhausted the monomer droplets also transfer via the aqueous phase into the micelles. The micelles, now containing both polymer and monomer absorb more emulsifier molecules from solution. When the emulsifier concentration falls below its critical value inactive micelles will be unstable and they dissolve leaving the polymer particles swollen with monomers. If agitation is stopped at this stage monomer droplets will coalesce. Diffusion of monomer from the droplets into the micelles will keep the monomer concentration in the micelles fairly constant through the polymerisation.

At 50 to 80 percent conversion the monomer droplets must have completely disappeared and the polymerisation rate decreases at a steady rate as monomer concentration in the particles decrease.

According to Smith and Ewart[11,12] the rate of polymerisation (Rp) and the number average degree of polymerisation ($\bar{X}n$) are dependent on the number of growing polymer particles (N). The number of growing polymer particles (N) is in turn dependent on the initiator and emulsifier concentrations.

$$Rp = \frac{N\ Kp\ M}{2} \quad \text{.....(1)}$$

$$\bar{X}n = \frac{N\ Kp\ M}{Ri} \quad \text{.....(2)}$$

$$N \propto I^{2/5},\ E^{3/5} \quad \text{.....(3)}$$

where Kp is the propagation rate constant, Ri is the rate of initiation, $[M]$, I and E are monomer, initiator and emulsifier concentrations respectively. The equations fit approximately for polymerisation of water insoluble monomers with a water soluble initiator.

1.4. Some Characteristics of Vinyl Acetate Emulsion Polymerisation

Although vinyl acetate can be polymerised in bulk, solution and suspension the emulsion polymerisation process is by far the major method of polymerisation. The reason for this is the suitability of the emulsion for most of its applications. There are some major variations from the general theory of emulsion[21,22,23] polymerisation as described in the previous section. This is likely due to the appreciable solubility of vinyl acetate in water (2.5 percent at 20°C).

1.4.1. Initiator Systems

A number of initiators have been employed in the emulsion polymerisation of vinyl acetate. The most important are peroxides with a reducing agent and a persulphate[21,22,23]. With hydrogen peroxide initiator, control of pH is very important. The pH must be below 3.4 and the presence of a reducing agent is very important. The most important reducing agent is the ferrous iron. Redox systems have been used. These systems will contain the peroxide or persulphate with a reducing agent such as ferrous ion,[14] thiosulphate or bisulphite. Oil soluble initiators can be employed with a water soluble reducing agent. An advantage of this type of system is the controlled rate of radical formation which is made possible because of the heterogeneity of the initiation reaction.

1.4.2. Stabilisers

Emulsion stabilisation has been achieved with a number of emulsifying agents. These include soaps, polyelectrolytes such as sodium methacrylate and polyvinyl alcohol or a combination of these compounds. Emulsions with polyvinyl alcohol or any other protective colloid have been reported to have larger particle diameter[14] than emulsions with soap as the sole emulsifier. The emulsion viscosities are also higher when these protective colloids are employed. Higher stability to storage, frost, electrolyte and better pigment compatibly have been reported with these protective colloids[14]. The most important of these protective colloids for vinyl acetate polymerisation is polyvinyl alcohol. The work of Capitani and Pirrone and others[15,17] has shown that medium molecular weight partially hydrolysed polyvinyl acetate is most effective. The acetyl content of the polyvinyl alcohol varying from 12 to 20 percent gives the best results. The use of polyvinyl alcohol in conjunction with surfactants especially those with sulpho groups has been reported to give extra stability to polyvinyl acetate emulsions[4,16].

Chapter 2

SCOPE OF THE PRESENT INVESTIGATION

Polyvinyl acetate emulsions are used in the textile, paint and adhesive industries in Nigeria.

In the textile industry it is used for sizing and for finishing. It has considerable better water resistance than starch which is the most well known sizing and finishing agent. In the paint industry both homopolymer and copolymer emulsions are employed in gloss and emulsion paints. The adhesive industry is just expanding and it is envisaged that the use of polyvinyl acetate in this industry will be intensified.

The present major source of these emulsions in Nigeria is the Hoechst Industries Limited. This company supplies the industries and the supply is usually supplemented with import from overseas.

Most methods of preparation of polyvinyl acetate emulsions are patented and are difficult if not impossible to come by. This project is therefore designed to investigate the effect of the various additives in the emulsion polymerisation of vinyl acetate on the properties of the emulsion obtained with a view of coming out with possible formulations of desired properties.

The molecular weight of dispersed polymer, viscosity and stability of the emulsion, determine the ultimate suitability of the given product for the specific use. The effect of the various additives on

these properties was therefore investigated. The effect on the yield was also investigated since this determines the economy of the process.

Most of the previous work on vinyl acetate emulsion polymerisation is with water soluble initiators such as sodium or potassium persulphate alone or with a reducing agent. In the present investigation a redox system consisting of an oil soluble initiator benzoyl peroxide and ferrous ion was used. It was hoped that a system like this would lead to a more gradual increase in initiation rate with conversion as compared to the constant initiation rates for water soluble initiators. The gradual increase in initiation rate will make it easier to control the molecular weight of the polymer product even without the addition of chain transfer agent. This has been proved right from the results of the present study.

An attempt was made to study the mechanical properties of the emulsion and polymer films to assess the effects of the additives in the polymerisation on the film properties.

Chapter 3

3. EXPERIMENTAL

3.1. Materials

3.1.1. Recrystallisation of the Benzoyl Peroxide Initiator

A saturated solution of benzyol peroxide initiator (BDH reagent) was made in chloroform. The solution was filtered and the filterate transfered into a clean beaker. To the filterate twice the volume of methanol was added and the crystals allowed to form. The crystals were filtered and dried on a filter paper. This was stored in a dessicator over silica gel and stored in a refrigerator until needed.

3.1.2. Purification of Vinyl Acetate Monomer

The vinyl acetate (BDH reagent and some commercial grade donated by Nigerian Hoechst Limited, Lagos) was washed with 10 percent sodium hydroxide solution in a separating funnel. This was to remove the hydroquinone inhibitor. The washing was repeated many times until a clear aqueous layer was obtained. The vinylacetate was then washed with distilled water to remove any trace of the alkali. The washed monomer was then dried by shaking with few grams of anhydrous sodium sulphate. After drying a few grams of cuprous chloride inhibitor was added and the monomer distilled under vacuum. The distillate was collected and stored in a refrigerator until needed.

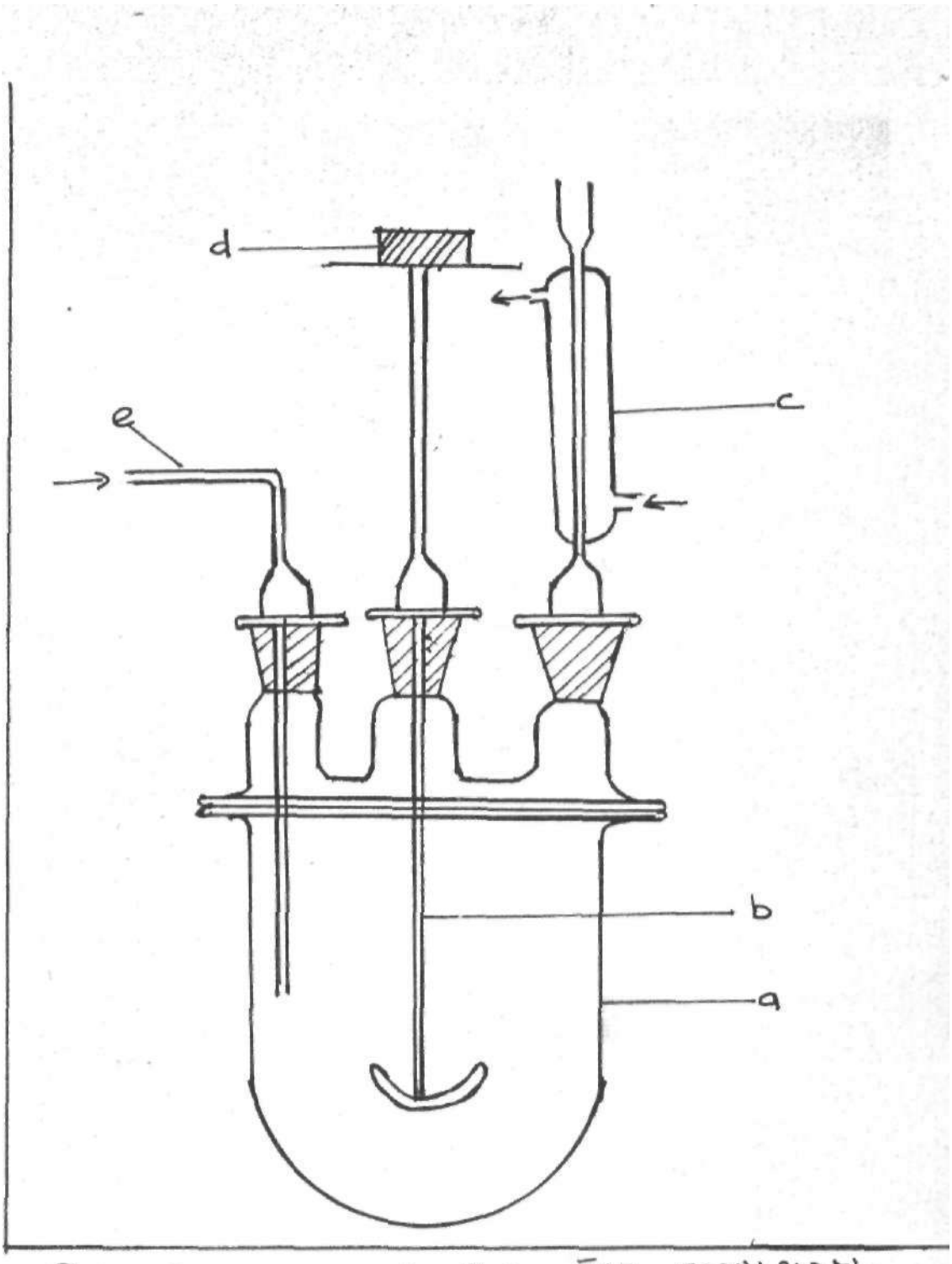


FIG. 2 APPARATUS FOR THE EMULSION POLYMERISATION OF VINYL ACETATE

(a) REACTION KETTLE (b) STIRRER

(c) CONDENSER (d) STIRRER MOTOR

(e) NITROGEN INLET

Other materials used are of BDH grade except where it is specified to be otherwise. The polyvinyl alcohol used has a molecular weight average ($\bar{M}n$) of 40,000 corresponding to an average degree of polymerisation of approximately 465.

The acetehyl content is approximately 2 percent.

3.2. Methods

3.2.1. Emulsion Polymerisation.

The set up for the polymerisation is as shown in fig. 2. A 250 ml reaction kettle was used. For each polymerisation 40g of purified vinyl acetate was used. Three types of emulsifiers were used namely sodium lauryl sulphate, sodium stearate and polyvinyl alcohol. A mixed system consisting of polyvinyl alcohol and sodium lauryl sulphate was also used. All polymerisations were carried out at $40^{\circ}C \pm 1$ and the mixture was blanketed with nitrogen that has been passed through alkaline pyrogallol to remove any trace of oxygen which can inhibit the reaction.

The typical recipe is given below.

Vinyl acetate	- 40g
Distilled water	- 80g
Benzoyl peroxide	- 0.1g
Ferrous ammonium sulphate hexahydrate	- 0.28g
Sodium pyrophesphate decahydrate	- 1.2g

The type and quantity of emulsifying agent were varied. The time of polymerisation was also varied. The aim was to get products of

different molecular weights and emulsions with different characteristics. The emulsions so prepared were labelled A_1 - A_{18} (Table 3).

Table 3

The Experimental conditions that were varied in the Preparation of the emulsions labelled A_1 - A_{18}

Emulsion	Emulsifying agent	Concentration of emulsifying agent % of monomer wt.	Time of polymerisation hrs.
A_1	Sodium lauryl sulphate	5.0	0.5
A_2	"	5.0	1.0
A_3	"	5.0	2.0
A_4	"	5.0	3.5
A_5	"	5.0	5.0
A_6	"	12.5	0.5
A_7	"	12.5	1.0
A_8	"	1.25	2.0
A_9	"	3.75	2.0
A_{10}	"	7.5	2.0
A_{11}	"	10.0	2.0
A_{12}	"	12.5	2.0
A_{13}	"	15.0	2.0
A_{14}	Sodium stearate	5.0	3.50
A_{15}	Polyvinyl alcohol and sodium lauryl sulphate	5:0.5	3.50
A_{16}	"	5:0.5	1.50
A_{17}	Polyvinyl alcohol	5.0	2.0
A_{18}	"	5.0	18.0

3.2.2. Separation of Polymer from the Emulsion.

The emulsion from the polymerisation was divided into two equal halves. One half was kept and the other half coagulated by addition of a 10M hydrochloric acid solution. The coagulated polymer was washed with water to free it from the soap. It was dissolved in methanol and reprecipitated with water. It was dried in the vacuum oven at a temperature of $40^{\circ}C \pm 1$ till a fairly constant weight was obtained. The polymeers obtained were labelled $P_1 - P_{18}$ corresponding to emulsions labelled $A_1 - A_{18}$. The yield was calculated and expressed as percent of original monomer weight. The results obtained are shown in Tables (4 to 6).

3.2.3. Viscosity Measurement and Molecular Weight Determination of the Polymer.

A one percent solution of the dried polymer was made in benzene (AR grade). The relative viscosities of varying concentrations of polymer were taken at $30^{\circ}C \pm 0.2$ using an Ubbelohde type of viscometer. (Table 8). A plot of reduced viscosity $\eta_{sp/c}$ against concentration was made. The limiting viscosity numbers $[\eta]$ were determined from the plots Fig. (5,6,7).

η_{sp} is the specific viscosity and c is the concentration of polymer in gram per decilitre of solution. The viscosity average molecular weight ($\bar{M}v$) was calculated from the equation

$$[\eta] = k\bar{M}v^{\alpha} \quad \ldots\ldots(4)$$

where k and α are constants. Their values at 30°C for polyvinyl acetate-benzene system are

$$k = 2.24 \times 10^{-4} \text{ decilitre per gram. (24)}$$

$$\alpha = 0.65$$

The results are shown in Tables 9 - 11.

3.2.4. Determination of the Emulsion Viscosity.

This was determined using a rotation type Viscometer Contraves Epprecht Rheomat 15. The viscosity of the stable emulsions was found to be almost constant at 1.03 centipoise per second (Tables 4 - 6).

3.2.5. Film Casting from the Emulsion.

The casting of the emulsion film was done using a petri dish. A 10 cm^3 of the emulsion was placed in the dish and the dish kept on a flat surface. The emulsion was left to dry under laboratory conditions. (25°C and 65% relative humidity). After 24 hrs. the film was removed for tensile tests. It was found that the films were too brittle for any tensile tests to be performed satisfactorily. Plasticisation was therefore necessary.

3.2.6. Plasticisation of the Emulsion.

The plasticiser used is 90 percent solution of dibuty phthalate in methanol. It was incorporated at 10 and 5 percent level based on the polymer.

After adding the required amount of plasticiser the mixture was vigorously stirred to ensure proper mixing. 10 cm^3 of the plasticised emulsion was again placed in a petri dish and the emulsion film allowed to form under the same conditions as described in the previous section.

3.2.7. Film Casting from Polymer Solution.

A 5 percent solution of the polymer which has been separated from the emulsion was made in chloroform. The film was cast on mercury surface using 20 cm^3 of the solution. The resulting polymer film was left to dry under the same conditions as described earlier. The films were removed after 24 hours and labelled P_1 - P_{18} corresponding to polymer samples labelled P_1 - P_{18}.

3.2.8. Determination of Relative Emulsion Stability.

The emulsion stability was assessed using two qualitative methods.

(1) The ease of separation on storage in a stoppered bottle under the laboratory conditions. (2) The ease of separation by coagulation using concentrated hydrochloric acid solution. The emulsions that separated out immediately the agitation was stopped were labelled poor. Emulsions which were easily coagulated with hydrochloric acid solution but separated on storage only after a day were labelled fairly stable. The emulsions labelled stable were not coagulated with hydrochloric acid addition and separation on storage was noticed only after a week or more. (Tables 4 - 7).

3.3. Measurement of Tensile Properties of the Films.

The stress-strain characteristics of the films were determined using the Instron tensile testing machine Table model 1026. The machine operates at constant rate of strain. The instrument has a load weighing capacity of 0-500kg. The crosshead and chart speeds range from 50 to 500 mm/min. The crosshead speed and chart speed depend on the extension the specimen can undergo and also on the cell selected. The chart magnification is fixed by the chart to crosshead speed ratio.

3.3.1. Tensile Properties of the Emulsion Films.

The gauge length of the test sample was fixed at 2.0 cm. The thickness was measured accurately using a micrometer screw gauge. The sample width was fixed at 1.0 cm. The machine was set with the given specifications.

Load cell	1026BM (500g - 2000g)
Full scale reading	1,000g
Chart speed	50 mm/min
Crosshead speed	50 mm/min
Chart magnification factor	1

From the load - extension curve recorded the breaking load and extension at break were noted. The breaking stress and percentage elongation were calculated as shown.

$$\text{Breaking stress} = \frac{\text{Breaking load (kg)}}{\text{Cross sectional Area } (m^2)} \quad \ldots\ldots(5)$$

$$\% \text{ elongation} = \frac{\text{chart reading of extension}}{\text{magnification factor}} \times \frac{1 \times 100}{\text{gauge length}} \quad (6)$$

3.3.2. Tensile Properties of the Polymer Film.

The tensile properties of an emulsion film is affected by the additives present in the emulsion. It was therefore thought necessary to study the tensile properties of the film obtained from the polymer that has been separated from the emulsion and if possible, compare the results obtained with those obtained for the corresponding emulsion films.

The gauge length and width of the test samples were fixed at 2.0 and 1.0 cm respectively. The film thickness was measured accurately with a micrometer screw gauge. The instron setting was modified because of the lower breaking stress and higher percentage elongations as compared to the emulsion films.

The machine specifications are as shown

Load cell	1026BM (500g-2,000g)
Full scale reading	500g
Chart speed	50 mm/min
Crosshead speed	200 mm/min
Chart magnification factor	0.25

The breaking stress and the percentage elongation were calculated using the equations described earlier. (Equations 5 and 6).

Chapter 4

4.0 RESULTS AND DISCUSSION

4.1. Nature of Polyvinyl acetate Emulsion obtained under different Experimental conditions.

The results presented in Tables 4 to 7 show the effect of emulsifying agent and its concentration as well as of time of polymerisation on the colour, yield and viscosity of emulsion and its relative stability on storage and to mineral acid.

Table 4

Effect of different emulsifying agents on the emulsion properties

Time of polymerisation - 3½hrs.

Concentration of emulsifier in % monomer weight - 5

Emulsion	Name of emulsifier	Colour of emulsion	Relative stability of emulsion	Polymer yield from the emulsion %	Viscosity of the emulsion
A_4	Sodium lauryl sulphate	white	Poor	68.5	
A_{14}	Sodium stearate	orange	Poor	18.3	
A_{15}	*Polyvinyl alcohol and sodium lauryl sulphate	white	Fairly stable	19.4	1.03cp/s
A_{18}	Polyvinyl alcohol	white	Stable	Very small	1.03cp/s

* The concentrations of polyvinyl alcohol and sodium sulphate are 5 and 0.5 percent respectively.

Table 5

Effect of varying emulsifier concentration on the emulsion properties

Emulsifying agent - Sodium lauryl sulphate

Time of polymerisation - 2hrs.

Emulsion	Emulsifier concentration	Relative stability of the emulsion	Polymer yield from the emulsion %	Viscosity of the emulsion
A_8	1.25	Fairly stable	9.9	1.03cp/sec
A_9	3.75	Fairly stable	17.4	1.03cp/sec
A_3	5.0	Poor	47.6	-
A_{10}	7.5	Fairly stable	15.9	1.03cp/sec
A_{11}	10.0	Fairly stable	20.3	1.03cp/sec
A_{12}	12.5	Poor	48.5	-
A_{13}	15.0	Poor	49.2	-

Table 6

Effect of Time of Polymerisation on the emulsion properties

Emusifying agent - 5% Sodium lauryl sulphate on monomer weight

Emulsion	Time of Polymerisation hrs.	Relative stability of the emulsion	Polymer yield from the emulsion %	Viscosity of the emulsion
A_1	0.5	Fairly stable	13.1	1.03cp/sec
A_2	1.0	Fairly stable	26.2	1.03cp/sec
A_3	2.0	Poor	47.6	-
A_4	3.5	Poor	68.5	-
A_5	5.0	Poor	83.1	-

Table 7

The ease of Polymer Separation from the Emulsion by addition of mineral acid

Time of polymerisation - 3½hrs.

Emulsifier concentration - 5% of monomer weight

Emulsion	Emusifying agent	Ease of coagulation with hydrochloric acid
A_4	Sodium laury sulphate	Fast
A_{14}	Sodium stearate	Fast
A_{15}	Polyvinyl alcohol + sodium lauryl sulphate	Fast
A_{18}	Polyvinyl alcohol	No effect

4.1.1. Colour of the Emusion.

As can be seen from Table 4, all the emulsifying agents used gave white emulsions except sodium stearate which gave an orange coloured emulsion. The orange colour with sodium stearate may be due to impurities in the sodium stearate used.

4.1.2. Polymer yield from the Emulsion.

(i) Effect of Emulsifying agent on the Polymer yield

Ionic emulsifying agents.

The work of Saito[28] on the binding of anionic emulsifiers to nonionic polymers show that besides the long chain nonpolar part of the emulsifier the ionic substituent adjacent to it also may play a significant role.

The presence of ionic groups on the emulsifier will aid micelle formation and this in turn will facilitate the solubilisation of monomer and polymer molecules in the hydrophobic part of the micelle. Two anionic emulsifiers were used. They are sodium lauryl sulphate and sodium stearate whose structures are shown below.

$CH_3(CH_2)_{16}\ COO^{\ominus}\ Na^+$ - Sodium stearate

$CH_3(CH_2)_{11}\ -O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{\ominus}\ Na^+$ - Sodium lauryl sulphate

Both emulsifiers have potential ionisable groups. In the case of sodium stearate this is the weak carboxylate groups which can be ionised to carboxylate anion at a high pH whereas in the case of sodium lauryl sulphate which has a stronger acid group inisation is possible at a much lower pH. In vinyl acetate polymerisation the pH of the medium is about 5. It is likely that in the case of sodium stearate emulsifier, all the carboxylate groups were not fully ionised and hence did not aid micelle formation whereas in the case of sodium lauryl sulphate even at the low pH of the polymerisation medium the sulphate groups will be fully ionised and this will aid micelle formation. This explains why the yield is much higher for sodium lauryl sulphate as compared to sodium stearate (Table 4).

Non ionic emulsifying agent

Polyvinyl alcohol is used as a protective colloid to stabilise polymer emulsions. During the polymerisation it prevents coalescing of monomer droplets as well as of polymer particles. It aids in increasing the viscosity of the emulsion and also acts to a certain extent as an emulsifying agent. Polyvinyl alcohol has weakly acidic hydroxyl groups and will ionise only at a highly alkaline pH. Hence the usefulness of polyvinyl alcohol as emulsifying agent is limited. In the present investigation the pH of the medium was close to neutral. Polyvinyl alcohol under this acidic conditions will hardly be ionised and hence will not aid micelle formation. It is not surprising therefore that the yield of the polymer using polyvinyl alcohol alone as emulsifying agent was the minimum. Also, the polyvinyl alcohols used in emulsion polymerisations are partially hydrolysed. The solubilising power of the micelles of polyvinyl alcohol if it at all they ever[25] form will also depend on the hydrophobic acetyl content and the molecular weight of the partially hydrolysed polyvinyl alcohol[15,34]. The optimum acetyl content of partially hydrolysed polyvinyl alcohol used in emulsion polymerisation as reported in literature[17] is between 8 and 20 percent and medium range molecular weight. In the present investigation the only available polyvinyl alcohol which was used has an acetyl content of 2 percent and a low molecular weight range. This is another reason for the very poor yield with the polyvinyl alcohol used in the present study.

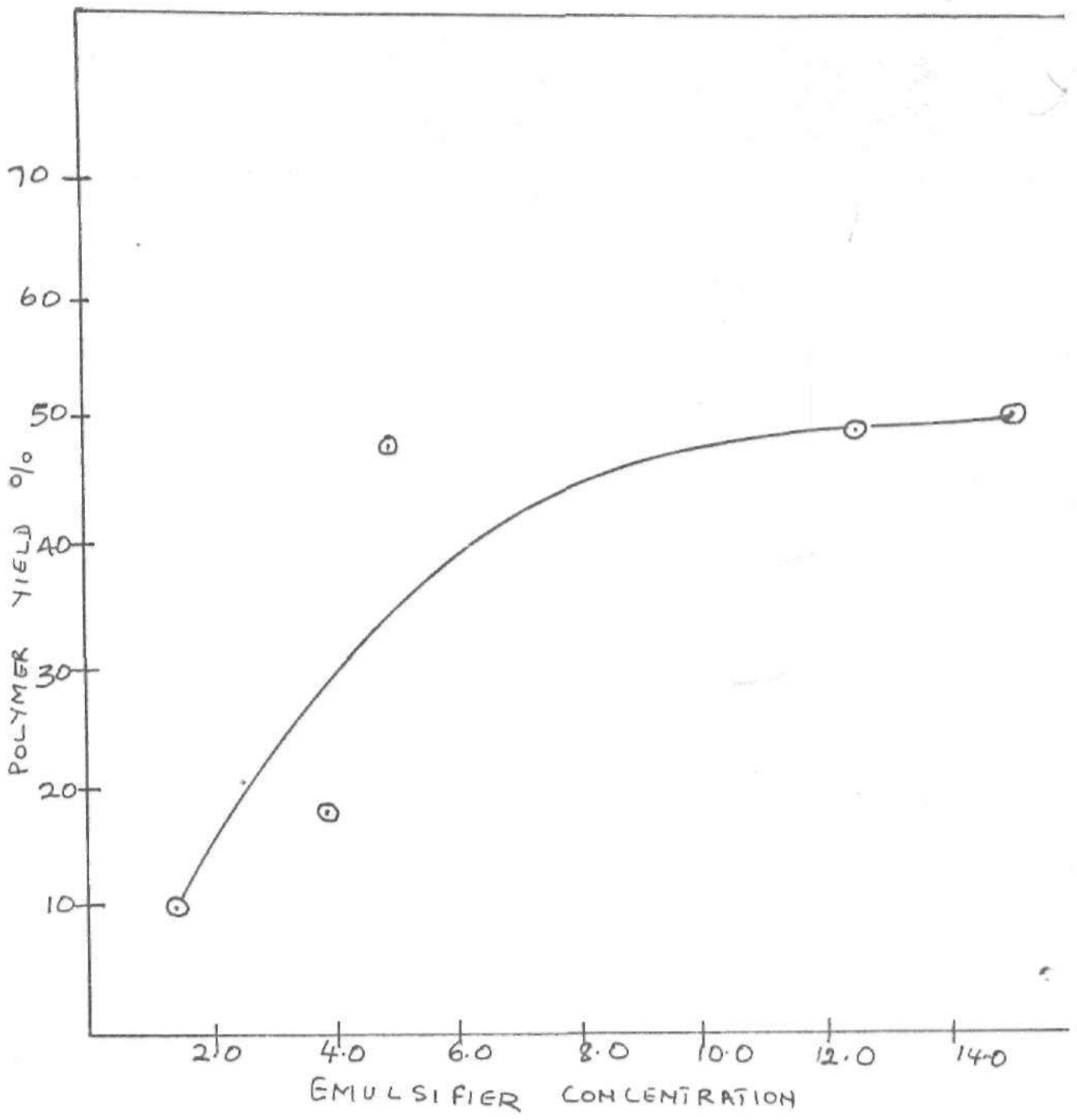


Fig.3 Effect of emulsifier concentration on the polymer yield

(ii) Effect of emulsifier concentration on the polymer yield.

The results in Table 5 and Fig. 3 show the effect of emulsifier concentration on the polymer yield. It can be seen that the polymer yield generally increased with increasing emulsifier concentration and levelling off at about 10% emulsifier concentration. The studies were made using sodium lauryl sulphate as emulsifier and its concentration varied from 1.25 to 15% while the time of polymerisation was kept constant. The abnormally low yield obtained with 7.5 and 10 percent emulsifier concentration may be due to inhibitors such as oxygen which might have increased the induction period given the low yield. If the polymerisation reactions were carried out for longer periods it would have been possible to eliminate the effect of this induction period and see clearly the effect of emulsifier concentration on the polymer yield.

According to Smith and Ewart[11,12] the rate of an emulsion polymerisation R_p is

$$R_p = \frac{N k_p M}{2} \quad \text{.....(3)}$$

where M is the micellar monomer concentration N is the number of polymer particles and k_p is the propagation rate constant. The number of polymer particles increases with emulsifier concentration (E) and for an ideal system

$$N \propto E^{3/5}$$

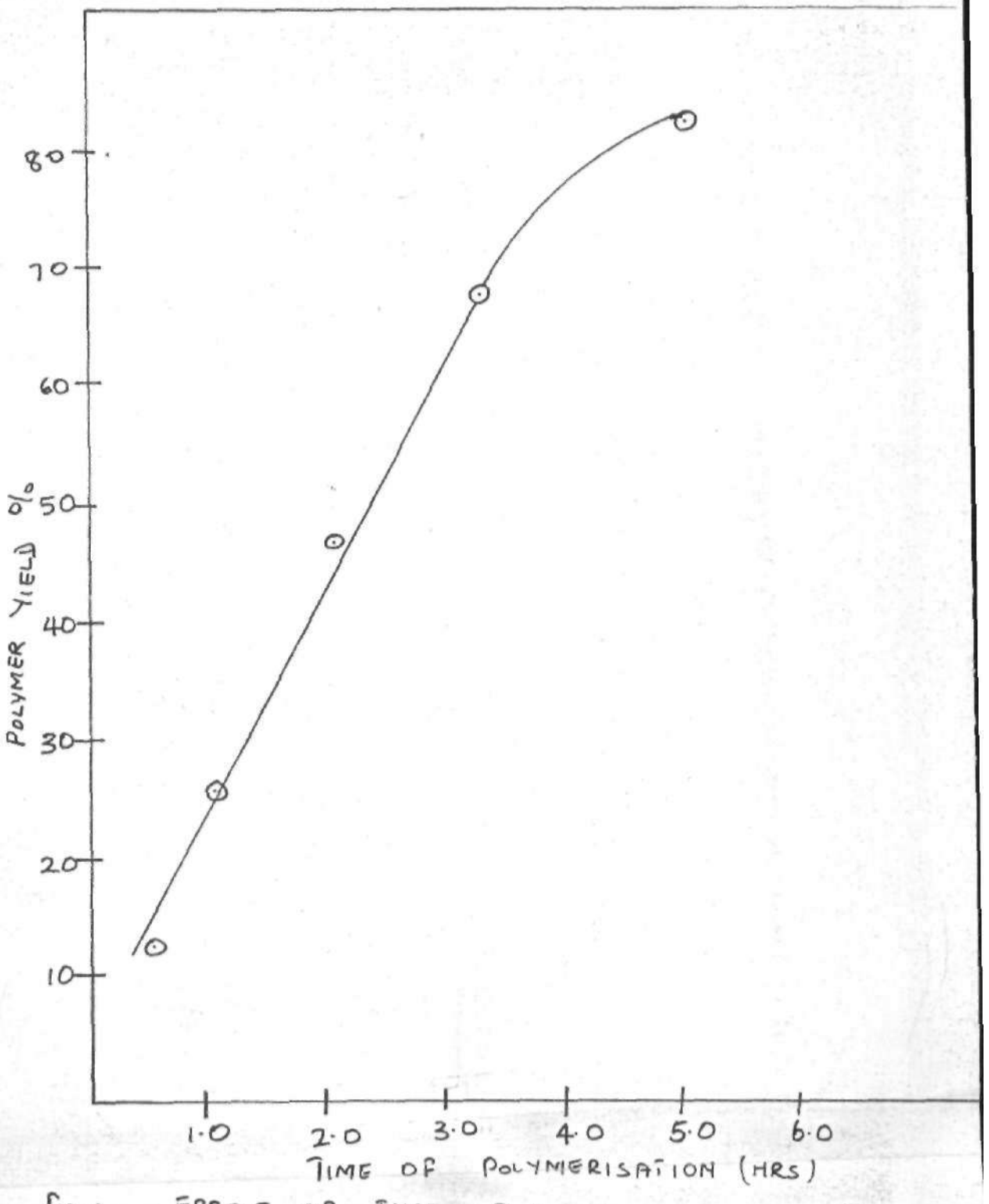


fig 4. EFFECT OF TIME OF POLYMERISATION ON THE POLYMER YIELD.

This increase in number of polymer particles with emulsifier concentration explains the increase in yield with emulsifier concentration at the constant time of polymerisation.

(iii) Effect of time of polymerisation on the polymer yield.

The investigation was carried out using 5 percent sodium lauryl sulphate as emulsifier and the time varied from 0.5hr to 5hrs. The results are given in Table 6 and illustrated in Fig. 4.

It can be seen from Fig. 4 that the polymer yield increased with the time of polymerisation. This is as expected.

For a typical free radical polymerisation initiated chemically as in the present study the rate of polymerisation is first order with respect to monomer. The rate of polymerisation decreases with monomer concentration as indicated in the expression

$$R_p = k_p \left(fk_d I / k_t\right)^{\frac{1}{2}} M \quad \ldots\ldots\ldots(7)$$

Where R_p is the rate of polymerisation I is the initiator concentration, M is the monomer concentration, f is the initiator efficiency and k_p, k_t, k_d are rate constants for propagation, termination and dissociation of the initiator. The concentration of the monomer decreases with conversion and so also the rate of polymerisation should decrease with conversion.

In an emulsion polymerisation, the locus of polymerisation is in the micelles. Diffusion of monomer from solution and monomer

droptelts into these micelles will keep the micellar monomer concentration fairly constant throughout the polymerisation. A slight decrease in rate is observed only at high conversions when the monomer droplets are exhausted and the micellar monomer concentration decreases.

In the present study a constant rate of polymerisation was observed up to about 80 percent conversion. This is in good agreement with the theory. Friis and Hyhaven[27] studied the effect of time of polymerisation for varying concentrations of the emulsifier (2.4-24g/litre). This is lower than the emulsifier concentration used in the present study. The shape of the curve is similar except that it has a high slope and this is as expected since rate is expected to increase with increasing number of polymer particles which in turn increases with micelle concentration and hence on emulsifier concentration as indicated in equations 1 and 3.

$$R_p = \frac{N k_p M}{2} \qquad \ldots\ldots(1)$$

$$N \propto E^{3/5} \qquad \ldots\ldots\ldots\ldots(3)$$

4.1.3. Viscosity of the Emulsion.

The viscosity of the various emulsions prepared and found stable is recorded in Tables 4 - 6. The viscosity was fairly constant and has a value of 1.03 cp/sec.

The emulsion viscosity does not depend so much on the molecular weight and concentration of the dispersed polymer but on other factors such as the viscosity of the liquid phase, particle size, particle aggregation, emulsifier content and any other macromolecular substance dissolved in the liquid phase. It is worth while to point out here that the polymer polyvinyl acetate is present in the emulsion in the dispersed form and not in soluble form. It is only when the polymer dissolves in the solvent that even very low concentrations increase the viscosity markedly.

The viscosity value of 1.03 cp/sec is very low when compared with the viscosity of commercial polyvinyl acetate emulsions e.g. 60% solution of Mowillith 20 (homopolymer emulsion of vinyl acetate) product of the Hoechst industries has a viscosity of 20 poise per sec.[14] The low value as compared to commercial product is partly due to the low solid content of the emulsions which were found stable enough. The very high viscosity of the commercial sample may be due to other polymeric additives such as polyvinyl alcohol of very high molecular weight dissolved in the dispersing medium. The polyvinyl alcohol used in the present investigation as stated earlier is of very low molecular weight and this will not affect the viscosity of emulsion noticeably. This explains why the emulsion prepared with the polyvinyl alcohol available gave emulsion of same viscosity as those prepared with the soap emulsifier.

4.1.4. Stability of the Emulsion.

(i) Effect of emulsifying agent on the stability of the emulsion.

As shown in Table 4 the emulsion with polyvinyl alcohol was more stable than those emulsions prepared with sodium lauryl sulphate and sodium stearate emulsifiers. This is in agreement with results obtained by earlier workers. The higher stability of this emulsion however may not be due to the polyvinyl alcohol as stability is also related to the soild content of the emulsion. It has been found in the present investigation that the stability decreases with increasing solid content of the emulsion. The emulsion prepared with polyvinyl alcohol alone has the minimum solid content and this may be greatly responsible for the high stability of this emulsion.

Capitani Pirrone and Shirashi[15,17] have reported that the use of partially hydrolysed polyvinyl alcohol of medium molecular weight as protective colloid gives very stable emulsions of polyvinyl acetate. The optimum value of acetyl content according to these workers is between 8 and 20%. The polyvinyl alcohol used in the present studywere of low molecular weight and of low acetyl content (2 percent). The emulsions obtained were unstable after storage for over 8 days.

During the emulsion polymerisation of vinyl acetate the pH falls below 7[25]. Fatty acid soap such as sodium lauryl sulphate and sodium stearate form very stable emulsions under fairly alkaline conditions[18] but under these conditions the emulsions would be less stable. This accounts for the poor stability of the emulsions with

these two emulsifying agents.

(ii) Effect oe Emulsifier concentration and the time of Polymerisation on the stability of the emulsion.

As can be seen from Tables 5 and 6 it appears that the solid content of the emulsion is the factor that determines the relative stability of the emulsions. Even at very high emulsifier concentration the emulsions of fairly high solid content were not stable. The relative stability of the emulsion with 7.5 and 10 percent emulsifier concentration is likely due to the very low yield of polymer obtained for those concentrations of the emulsifier. A likely reason for this low yield has been given previously. The decrease in relative emulsion stability with the time of polymerisation is again a factor of increasing solid content of the emulsion as the polymerisation gets to very high conversions. Therefore the preparation of stable emulsions requires a balance between the yield and the concentration of the emulsifying agent.

(iii) Separation of Polymer by coagulation with mineral acid.

The results in Table 7 show that emulsions with sodium stearate and sodium lauryl sulphate were easily coagulated with concentrated hydrochloric acid solution. The reaction of the acid with the alkaline soap destroys the stabilising action of the soap. This explains why the emulsions with the fatty alkaline soap were easily coagulated with hydrochloric acid. Polyvinyl alcohol is neutral to

acid and this is why the emulsion with polyvinyl alcohol as sole stabiliser was not affected by the acid.

4.2. Molecular weight of the polymer.

The polymers from the emulsions A_1 - A_{16} were separated from the emulsions and dissolved in benzene. Viscosity determinations at various concentrations of the polymer were made and the data presented in Table 8(a-p).

Table 8

Determination of Limiting viscosity $[\eta]$ from viscosity measurements

(a) Sample P_1 t_o = 2.29 mins.

Concn. c g/100ml	Time (mins)	η_{rel} (t/t_o)	η_{sp}	η_{sp}/c
1.00	6.42	2.80	1.80	1.80
0.80	5.46	2.38	1.38	1.73
0.60	4.57	2.00	1.00	1.67
0.50	4.18	1.83	0.83	1.66
0.40	3.75	1.64	0.64	1.60
0.20	2.98	1.30	0.30	1.50

(b) Sample P_2 t_o = 2.29 mins.

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	6.13	2.68	1.68	1.68
0.80	5.13	2.24	1.24	1.55
0.60	4.30	1.88	0.88	1.47
0.50	3.90	1.70	0.70	1.40
0.40	3.50	1.53	0.53	1.33
0.20	2.86	1.25	0.25	1.25

(c) Sample P_3

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	5.57	2.43	1.43	1.43
0.80	4.73	2.07	1.07	1.34
0.60	3.98	1.74	0.74	1.23
0.50	3.60	1.57	0.57	1.14
0.40	3.31	1.45	0.45	1.13
0.20	2.76	1.20	0.20	1.00

(d) Sample P_4

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	4.80	2.10	1.10	1.10
0.80	4.26	1.86	0.86	1.08
0.60	3.67	1.60	0.60	1.00
0.50	3.40	1.48	0.48	0.96
0.40	3.17	1.35	0.38	0.95
0.20	2.71	1.18	0.18	0.90

(e) Sample P_5 t_o = 2.29 mins.

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	4.74	2.07	1.07	1.07
0.80	4.14	1.81	0.81	1.01
0.60	3.63	1.59	0.59	0.98
0.50	3.34	1.46	0.46	0.92
0.40	2.12	1.36	0.36	0.90
0.20	2.67	1.17	0.17	0.85

(f) Sample P_6

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	6.20	2.71	1.71	1.71
0.80	5.38	2.35	1.35	1.69
0.60	4.52	1.97	0.97	1.62
0.50	4.07	1.78	0.78	1.56
0.40	3.68	1.61	0.61	1.53
0.20	2.95	1.29	0.29	1.45

(g) Sample P_7

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	5.78	2.52	1.52	1.52
0.80	4.89	2.14	1.14	1.43
0.60	4.16	1.82	0.82	1.37
0.50	3.75	1.64	0.64	1.28
0.40	3.39	1.48	0.48	1.20
0.20	2.81	1.23	0.23	1.15

(h) Sample P_8 t_o = 2.29 mins.

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	4.39	1.92	0.92	0.92
0.80	3.93	1.72	0.72	0.90
0.60	3.44	1.50	0.50	0.83
0.50	3.20	1.40	0.40	0.80
0.40	2.97	1.30	0.30	0.75
0.20	2.61	1.14	0.14	0.70

(i) Sample P_9

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	4.67	2.04	1.04	1.04
0.80	4.15	1.81	0.81	1.01
0.60	3.55	1.55	0.55	0.92
0.50	3.32	1.45	0.45	0.90
0.40	3.10	1.35	0.35	0.88
0.20	2.66	1.16	0.16	0.80

(j) Sample P_{10}

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	4.98	2.14	1.14	1.14
0.80	4.30	1.88	0.88	1.10
0.60	3.75	1.64	0.64	1.07
0.50	3.43	1.51	0.51	1.02
0.40	3.18	1.39	0.39	0.98
0.20	2.72	1.19	0.19	0.95

(k) Sample P_{11} t_o = 2.29 mins.

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	4.75	2.07	1.07	1.07
0.80	4.16	1.82	0.82	1.03
0.60	3.61	1.58	0.58	0.98
0.50	3.39	1.48	0.48	0.96
0.40	3.13	1.39	0.39	0.98
0.20	2.73	1.19	0.19	0.95

(l) Sample P_{12}

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	6.06	2.65	1.65	1.65
0.80	5.64	2.20	1.20	1.50
0.60	4.18	1.82	0.82	1.37
0.50	3.79	1.66	0.66	1.32
0.40	3.44	1.50	0.50	1.25
0.20	2.79	1.22	0.22	1.10

(m) Sample P_{13}

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	6.17	2.69	1.69	1.69
0.80	5.19	2.27	1.27	1.59
0.60	4.29	1.87	0.87	1.45
0.50	3.87	1.69	0.69	1.38
0.40	3.51	1.53	0.53	1.33
0.20	2.85	1.24	0.24	1.20

(n) Sample P_{14} t_o = 2.29 mins.

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	3.96	1.73	0.73	0.73
0.80	3.52	1.55	0.55	0.69
0.60	3.20	1.40	0.40	0.67
0.50	3.00	1.31	0.31	0.62
0.40	2.85	1.24	0.24	0.60
0.20	2.55	1.11	0.11	0.55

(o) Sample P_{15}

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	-	-	-	-
0.80	4.61	2.01	1.01	1.20
0.60	3.85	1.68	0.68	1.08
0.50	3.50	1.53	0.53	1.00
0.40	3.19	1.39	0.39	0.93
0.20	2.68	1.17	0.17	0.85

(p) Sample P_{16}

c	t	t/t_o	η_{sp}	η_{sp}/c
1.00	5.22	2.28	1.28	1.28
0.80	4.43	1.93	0.93	1.13
0.60	3.80	1.66	0.66	1.08
0.50	3.56	1.55	0.55	1.08
0.40	3.23	1.41	0.41	1.00
0.20	2.71	1.18	0.18	0.90

The plots of viscosity number against concentrations are illustrated in Figs. (5,6,7). The values of limiting viscosity number obtained after the extrapolation of the viscosity number - concentration curves to zero concentration are given in Tables 9 to 11. The viscosity average molecular weight calculated from the Mark Hughin's equation

$$[\eta] = kM^{a} \quad \ldots\ldots(4)$$

are also given in the Tables 9 to 11.

Table 9

Effect of different emulsifying agents on the molecular weight of the polymer

Polymer	Emulsifier	Limiting viscosity $[\eta]$	$\bar{M}v \times 10^{-5}$
P_4	Sodium lauryl sulphate	0.86	3.27
P_{14}	Sodium stearate	0.51	1.46
P_{15}	Polyvinyl alcohol and sodium lauryl sulphate	0.66	2.17
P_{18}	Polyvinyl alcohol	-	-

Table 10

Effect of Emulsifier concentration on the molecular weight of the Polymer

Polymer	Emulsifier Concn.	Limiting viscosity $[\eta]$	$\bar{M}v \times 10^{-5}$
P_8	1.75	0.63	2.34
P_9	3.75	0.74	2.59
P_3	5.0	0.89	2.45
P_{10}	7.5	0.90	3.52
P_{11}	10.0	0.91	3.58
P_{12}	12.5	0.99	4.06
P_{13}	15.0	1.07	4.58

Table 11

Effect of Time of Polymerisation on the molecular weight of the Polymer

Polymer	Time of Polymerisation hrs.	Limiting viscosity $[\eta]$	$\bar{M}v \times 10^{-5}$
P_1	0.5	1.47	7.45
P_2	1.0	1.14	5.07
P_3	2.0	0.89	3.45
P_4	3.50	0.86	3.27
P_5	5.0	0.80	2.93

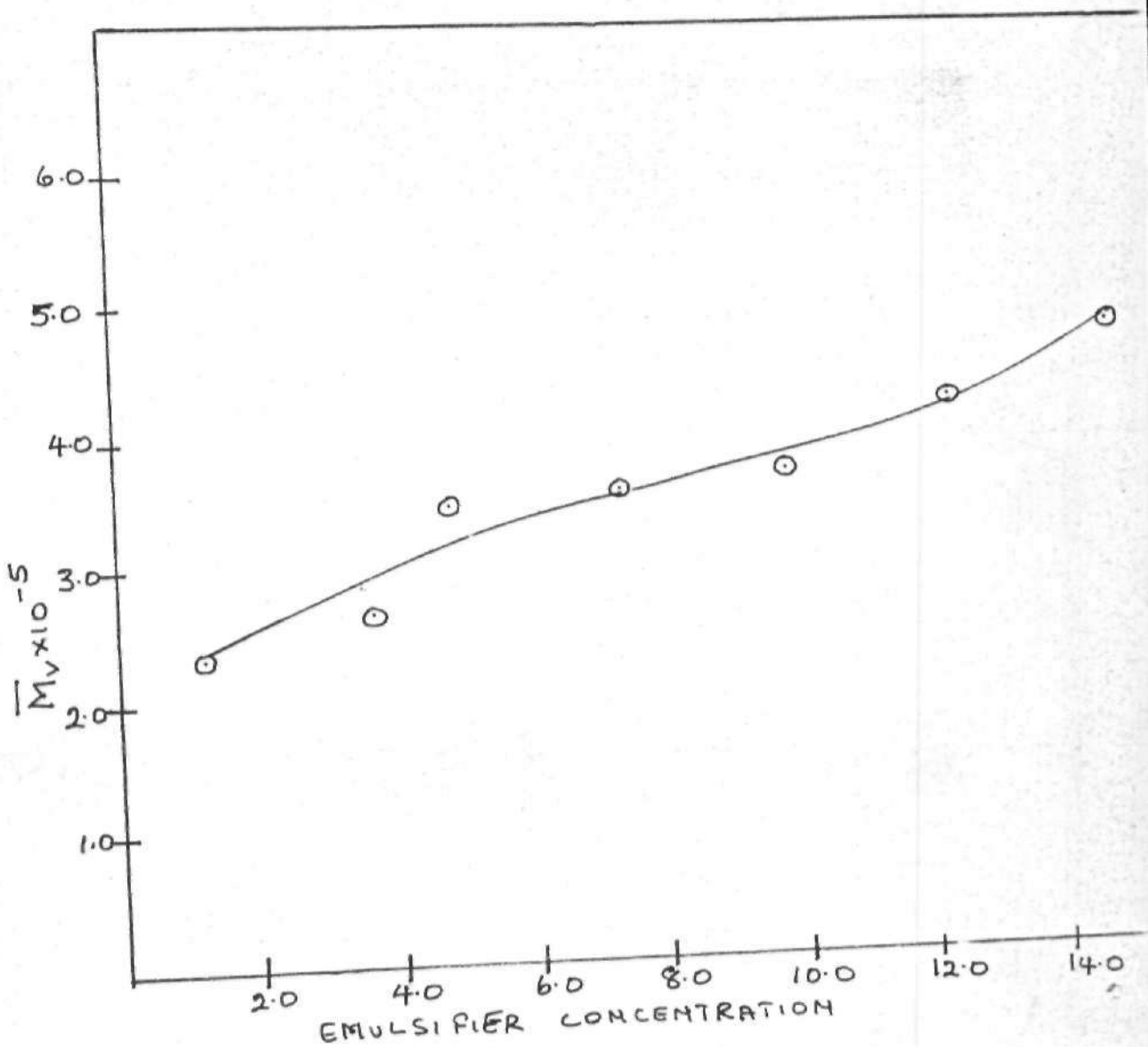


Fig 8. EFFECT OF EMULSIFIER CONCENTRATION ON THE MOLECULAR WEIGHT OF THE POLYMER.

(i) Effect of Emulsifying agent on the molecular weight of the Polymer.

The results in Table 9 show that the molecular weight of the polymer is highest with sodium lauryl sulphate as sole emulsifier. As explained earlier, this is due to the better binding of monomer-polymer particle to the emulsifier. The presence of ionisable groups on the emulsifier aids micelle formation and thus increases the micellar monomer concentration. This will in turn increase the average number degree of polymerisation ($\bar{X}n$) of the polymer as indicated by the expression below.

$$\bar{X}n = \frac{N k_p M}{R_i} \quad .....(2)$$

Increase in M the micellar monomer concentration will increase $\bar{X}n$ of the polymer.

The yield from the emulsion prepared with polyvinyl alcohol as sole emulsifier is extremely small and so no viscosity measurement on the polymer solution was possible.

(ii) Effect of Emulsifier Concentration on the Molecular weight of the Polymer.

The results in Table 10 and Fig. 8 show that molecular weight increases with emulsifier concentration. Increase in the emulsifier concentration (E) increases, N the number of active micelles as given in the equation

$$N \propto E^{3/5} .....(3)$$ for a system where Smith-Ewart theory is applicable. Since $\bar{X}n$ increases with N it is

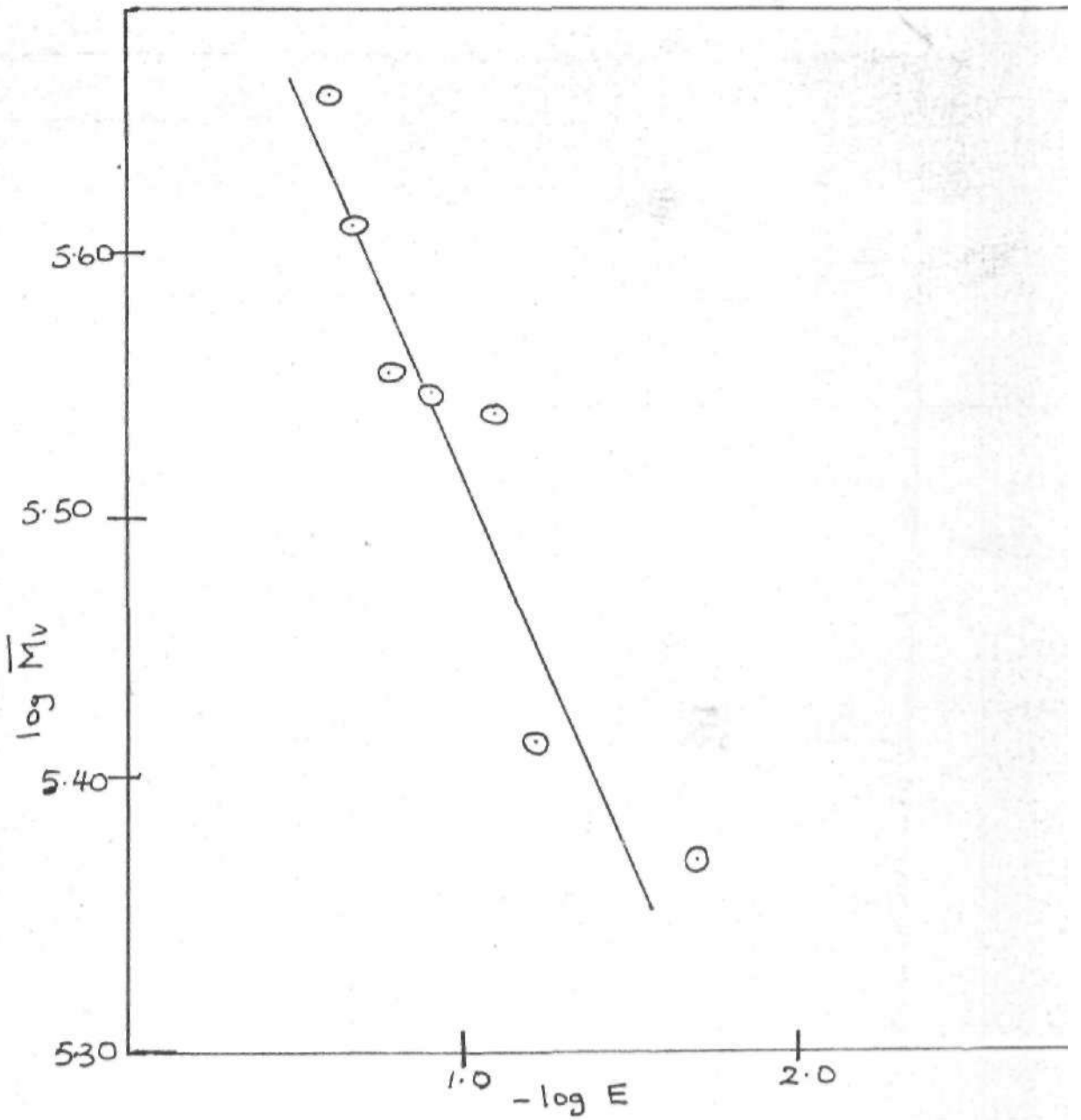


FIG 9 DEPENDENCE OF MOLECULAR WEIGHT ON EMULSIFIER CONCENTRATION

in order for molecular weight to increase with emulsifier concentration.

A plot of log $\bar{M}v$ against log E (Fig. 9) confirms the dependence of molecular weight on emulsifier concentration. The slope of the plot suggests that for this system molecular weight is proportional to 0.24 power of the emulsifier concentration Friis and Nyhagen using a persulphate initiator for the emulsion polymerisation of vinyl acetate at 50°C get a value of 0.5 for the index. The lower value obtained for the index in the present study may be due to the initiator system. Benzoyl peroxide is non ionic and will not aid micelle formation. Potassium persulphate is highly ionic. It will therefore aid micelle formation and help stabilise the emulsion. For same emulsifier concentration the number of active micelles with a persulphate initiator will be more than for the benzoyl peroxide initiator. This higher value of N (for same emulsifier concentration) which is possible with the persulphate initiator accounts reasonably well for the higher value of the index with the persulphate initiator as compared with the benzoyl peroxide initiator system used in the present study (Table 12).

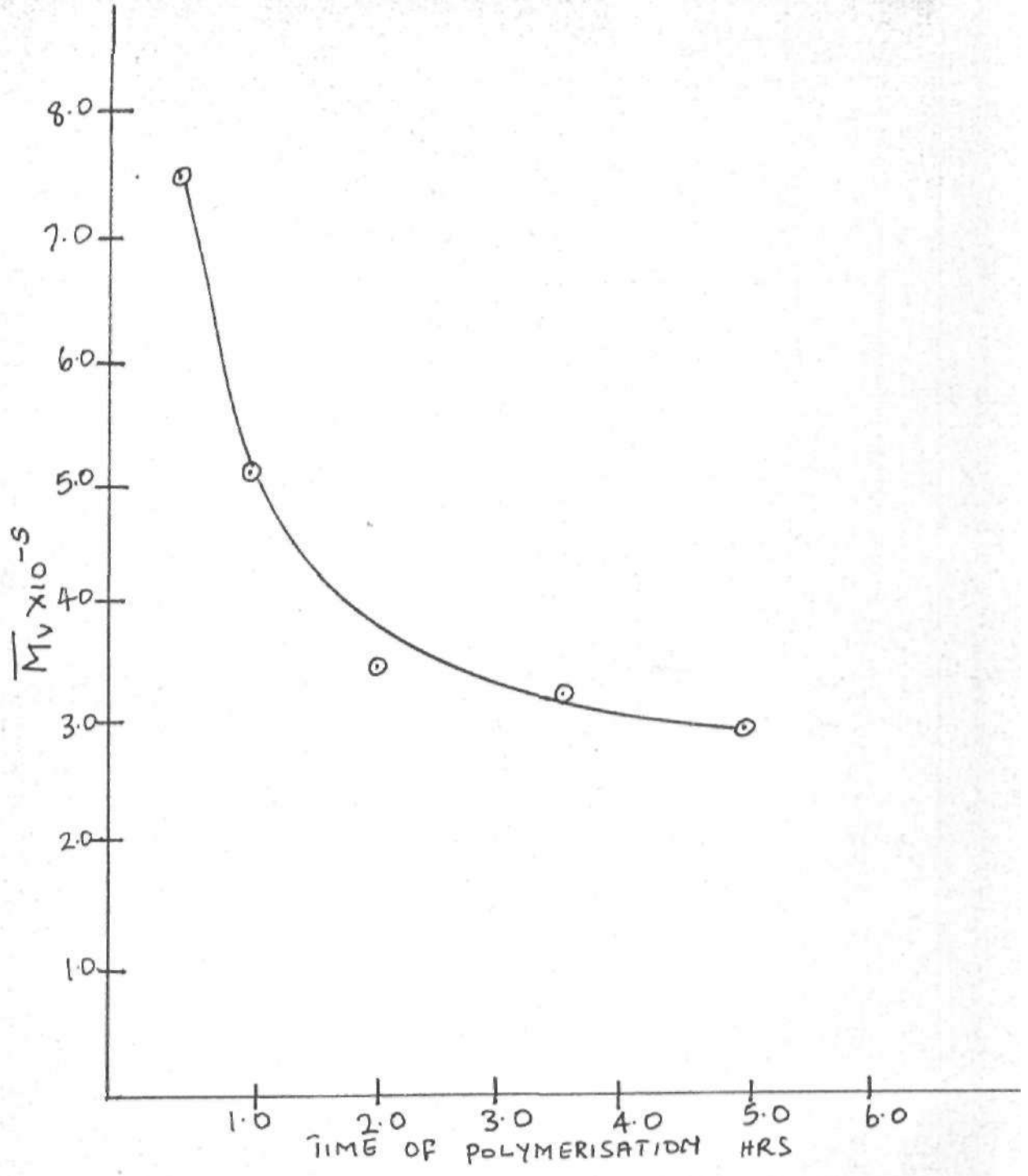


FIG 10 EFFECT OF TIME OF POLYMERISATION ON THE MOLECULAR WEIGHT OF THE POLYMER.

Table 12

Dependence of Molecular weight on Emulsifier Concentration

Emulsifier Concentration		Mv x 10^{-5}	-log (E)	log Mv
% of monomer weight	mole/litre H_2O [E]			
1.25	.021	2.34	1.6778	5.3692
3.75	.063	2.59	1.2007	5.4133
5.0	.084	3.45	1.0757	5.5378
7.5	.126	3.52	0.8996	5.5465
10.0	.168	3.58	0.7747	5.5539
12.5	.210	4.06	0.6778	5.6085
15.0	.252	4.58	0.5986	5.6609

(iii) Effect of Time of Polymerisation on the molecular weight of the Polymer.

As can be seen from the results in Table 11 and Fig. 10 the molecular weight decreases with time of polymerisation for the range

of time used in the study. The very rapid polymerisation possible at the high emulsifier concentration (25g/lire H_2O) may be responsible for the high molecular weight product obtained even after 30 minutes of polymerisation. A sharp decrease was observed after 30 minutes and a levelling off after 3 hours of polymerisation.

From the Smith-Ewart equation

$$\bar{X}n = \frac{N k_p M}{R_i} \quad .....(2)$$

the number average degree of polymerisation should increase with time of polymerisation as N the number of active micelles increase and M and R_i remain fairly constant. Infact this has been observed for vinyl acetate emulsion polymerisation using water soluble initiator like potassium persulphate[23,28]. With an oil soluble initiator like benzoyl peroxide the initiation rate (R_i) cannot be assumed constant and should be expected to increase with the time of polymerisation. The reaction of benzoyl peroxide and ferrous ion is a surface one and the rate of reaction should increase with stirring and prolonged contact between the two surfaces. This will explain why the molecular weight of the polymer decreases with time of polymerisation.

$$\bar{X}n = \frac{N k_p [M]}{R_i} \quad .....(2)$$

From the equation it follows then that increase in R_i will decrease $\bar{X}n$.

4.3. Tensile properties of the emulsion and polymer films.

4.3.1. Stree-strain properties of the emulsion films.

Stress-strain characteristics of the unplasticised as well as plasticised films from the emulsion were studied. The stress and the corresponding strain were calculated from the data obtained from the Instron tensile testing machine. They are given in Table 13 and illustrated in Fig. 11.

No satisfactory data could be obtained for the unplasticised film as it was very brittle. Emulsions were therefore plasticised with dibutyl phthalate in two different concentrations namely 10 percent and 5 percent based on the polymer weight estimated. The results were not reproduceable due to unsatisfactory method of plasticisation. It is very likely that plasticiser molecules are not evenly distributed. However the results are presented as they do show a general trend of stress-strain behaviour of plasticised emulsion films.

Table 13

Stress-strain properties of the emulsion film

(a) Sample A_8 Plasticiser content - 10% based on polymer

Load x 10^3 (kg)	Chart reading of extension (cm)	Stress x 10^{-5} (kg m^{-2})	Strain %
0	0	0	0
50	.4	.175	20
60	1.6	.210	80
80	3.2	.280	160
100	9.6	.350	480
120	11.2	.410	560
200	21.4	0.70	1070
240	23.2	0.82	1160
290	27.4	1.02	1370

(b) Sample A_8 Plasticiser content - 5%

Load x 10^3 (kg)	Chart reading of extension (cm)	Stress x 10^{-5} (kg m^{-2})	Strain %
0	0	0	0
50	0	0.17	0
100	0	0.34	0
150	0.25	0.51	12.5
200	0.4	0.68	20
190	1.6	0.65	80
190	4.6	0.65	230
250	7.6	0.85	380
400	10.4	1.36	520
500	11.8	1.70	590
560	12.4	1.94	620

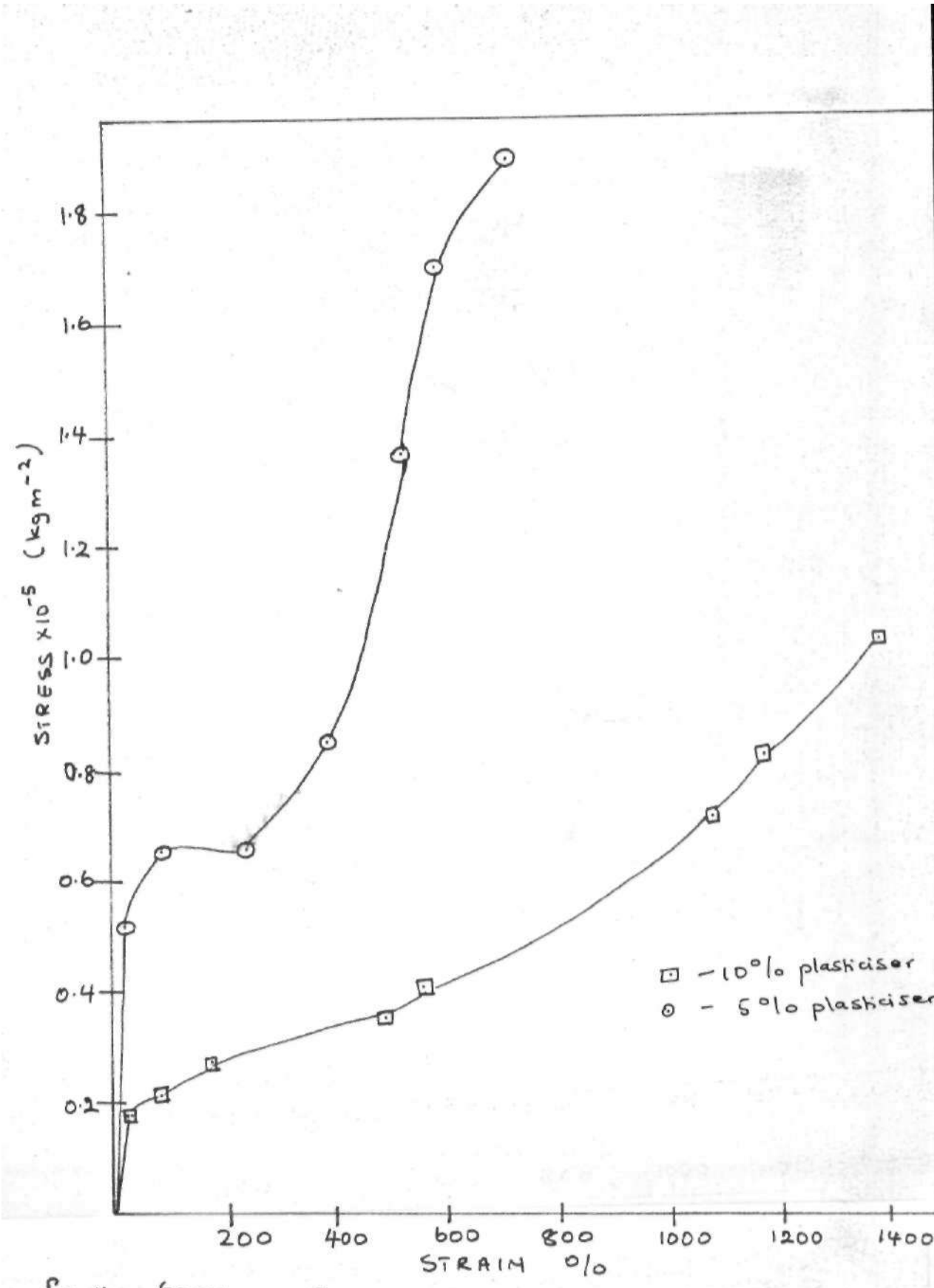


fig. 11 STRESS - STRAIN RELATIONSHIP FOR PLASTICISED EMULSION FILMS.

It can be seen from Fig. 11 that both the curves representing 5 percent and 10 percent plasticiser are 'S' shaped. Samples are hard initially and require extremely high stress for a small change in the strain. After this softening occurs and large strains are produced for very little change in the stress. At the latter stage pronounced hardening is observed until the sample finally breaks. With higher plasticiser content the curve is shifted to the right, the yield point is less defined and much flow is observed. Hardening is not as pronounced. A decrease in breaking stress with an increase in percentage elongation is observed with the high plasticiser concentration. (Fig. 11).

4.3.2. Stress-strain properties of the polymer film.

The brittle nature of the unplasticised emulsion film and the unsatisfactory results from the plasticised emulsion made the study on the polymer films very necessary. A study on the polymer film will also make it possible to eliminate the effects of the additives present in the emulsion on the properties of the film.

The polymer film was cast on mercury surface using 20 mls of a 5 percent solution of the polymer in chloroform. The films were transparent except for the film from the polymer obtained with sodium stearate as emulsifier which gave a brittle and transluscent film. As mentioned earlier the sodium stearate used might not be very pure.

The stress-strain characteristics of the polymer fimls was studied using the Instron tensile machine. The stress-strain data

are presented in Table 14 and illustrated in Figs. 12 and 13.

Table 14(a)

Stress-strain properties of films from polymer samples obtained with constant emulsifier concentration

Sample P_4 Time of polymerisation = $3\frac{1}{2}$ hrs.
$\bar{M}v = 3.27 \times 10^5$

Load x 10^3 (kg)	Chart reading of extension (cm)	Stress x 10^{-5} (kg m^{-2})	Strain %
0	0	0	0
25	0.1	.103	20
50	0.25	.206	50
75	0.8	.309	160
100	1.8	.412	360
150	2.45	.618	490
200	3.2	.824	640
250	4.1	1.03	820
260	4.6	1.07	920

Sample P_2 Time of polymerisation = 1.0hr. $\bar{M}v = 5.07 \times 10^5$

Load x 10^3 (kg)	Chart reading of extension (cm)	Stress x 10^{-5} (kg m^{-2})	Strain %
0	0	0	0
25	0.05	.089	10
50	0.15	.178	30
75	0.4	.267	80
100	0.9	.356	180
125	1.6	.445	320
150	2.1	.534	420
175	2.3	.623	460
200	2.5	.712	500
300	3.5	1.07	700
330	4.2	1.16	840

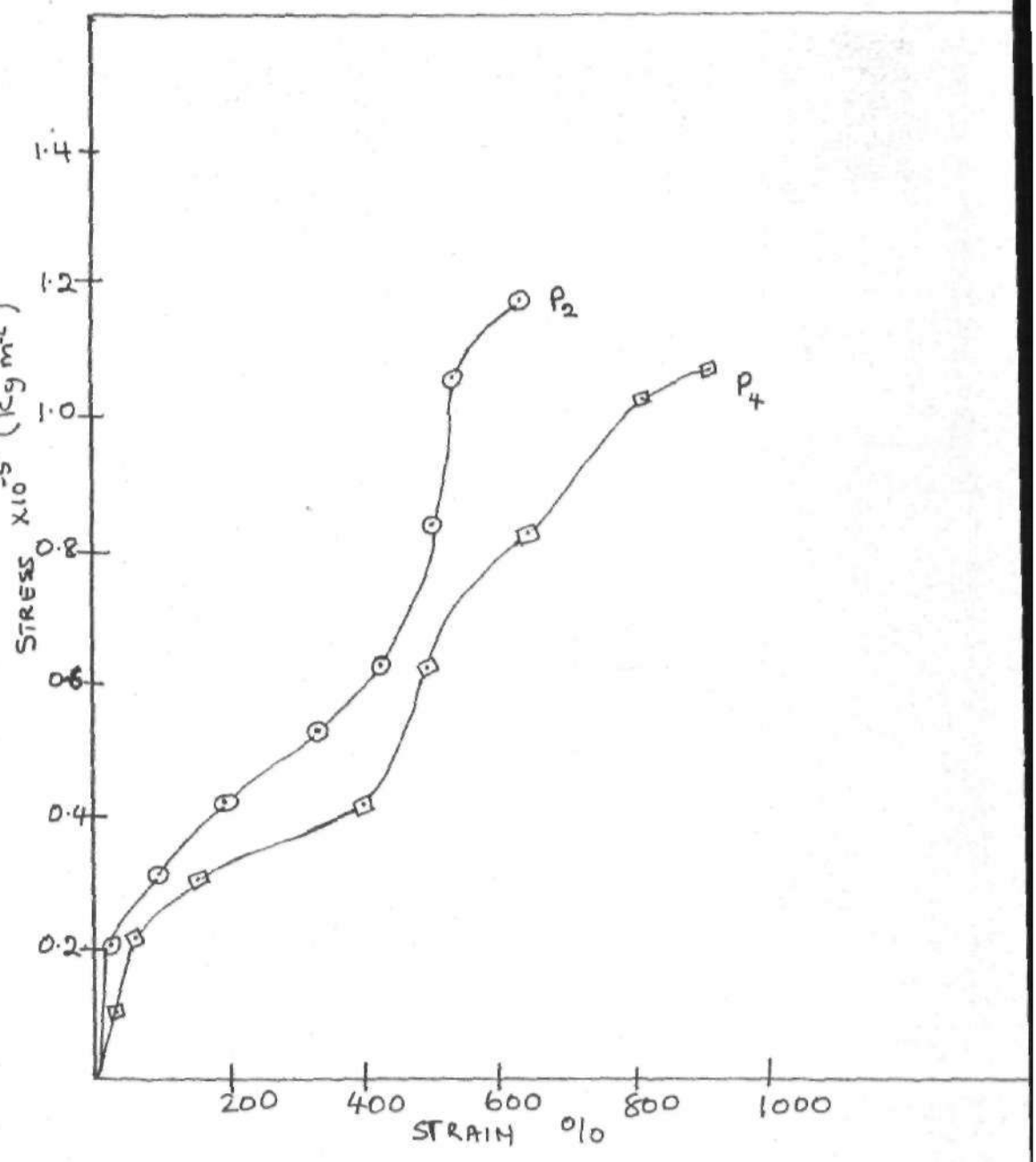


fig 12 STRESS- STRAIN RELATIONSHIP FOR POLYMER FILMS

Table 14(b)

Stress-strain properties of films from polymer samples obtained with varying concentration of emulsifier

Sample P_8 Emulsifier concentration = 1.25%

$\bar{M}v = 2.32 \times 10^5$

Load x 10^3 (kg)	Chart reading of extension (cm)	Stress x 10^{-5} (kg m^{-2})	Strain %
0	0	0	0
50	0.1	0.20	20
75	0.5	0.30	100
100	0.6	0.40	120
125	1.4	0.50	280
150	2.1	0.60	420
200	2.7	0.80	540
250	3.4	1.00	680
260	3.6	1.04	720

Sample P_{13} Emulsifier concentration = 15% $\bar{M}v = 4.58 \times 10^5$

Load x 10^3 (kg)	Chart reading of extension (cm)	Stress x 10^{-5} (kg m^{-2})	Strain %
0	0	0	0
25	0.05	.089	10
50	0.15	.178	30
75	0.4	.267	80
100	0.9	.356	180
125	1.6	.443	320
150	2.1	.534	420
175	2.3	.623	460
200	2.5	.712	500
300	3.5	1.07	700
330	4.2	1.16	840

The stress-strain behaviour resembles what has been described for the emulsion films. An important difference between the two is the softness and more rubbery nature of the polymer films.

4.3.3. Effect of molecular weight on the Stress-strain properties of the polymer films.

The molecular weight of the polymer has been varied using two methods.

(a) Varying the time of polymerisation using a constant concentration of the emulsifier.

(b) Varying the emulsifier concentration at a constant time of polymerisation.

The results of tensile tests obtained with these two sets of samples are presented in Table 14 and illustrated in Figs. 12 and 13.

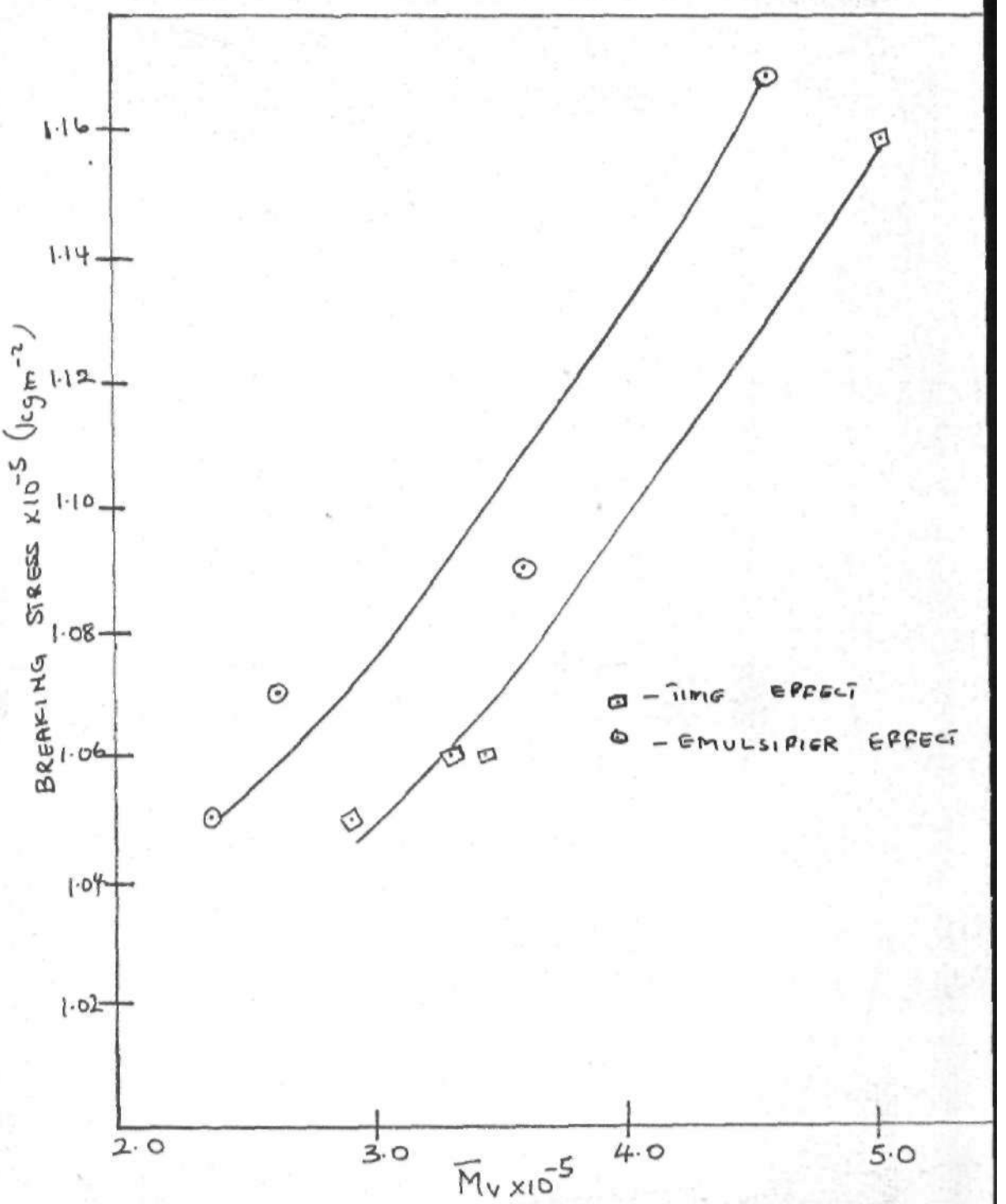
Figure 12 show the stress-strain relationship for two polymer samples under category (a) and figure 13 shows the stress-strain relationship for two polymer samples under category (b). From figure 12 it can be seen that for samples under category (a), strain percent increases with decreasing molecular weight for the same stress value. This is in order because long chain molecules can accommodate larger deformation through the rearrangement of the chains.

The results in Table 14b and figure 13 however show that for samples with higher molecular weight under category (b) the trend is reversed up to about 500 percent strain. The higher molecular weight sample gives higher strain under the same stress. An explanation

for this may be the higher quantity of emulsifier which can be adsorbed by the polymer from the high quantity of emulsifier used in the polymerisation. The adsorbed emulsifier molecules can act as plasticiser to increase the softness of the film.

A general effect of molecular weight of the polymer on the breaking stress and percentage elongation is presented in Table 15 and illustrated in Fig. 14. Higher values of breaking stress are recorded for samples under category (b) for the same molecular weight. It might be that the samples under category (b) have narrower molecular weight distribution.

The results in Table 15a show that for samples under category (a) the percentage elongation increases with decreasing stress and hence decreasing molecular weight. From table 15 (b) it can be seen however that for samples under category (b) the percentage elongation increases with molecular weight. The high emulsifier concentration used in the polymerisation to get the high molecular weight samples will increase the amount of adsorbed emulsifier markedly. The adsorbed emulsifier molecules will exercise some plasticising action giving the film a more rubbery nature. This will explain why for samples under category (b) the percentage elongation increases with increasing molecular weight of the polymer.



Fig·14 EFFECT OF MOLECULAR WEIGHT ON THE BREAKING STRESS OF POLYMER FILMS

Table 15

Effect of molecular weight on the tensile properties of the polymer film

(a) Emulsifier concentration 5% sodium lauryl sulphate. Time of polymerisation varied from 1hr. to 5 hrs.

Sample	Mv x 10^{-5}	Breaking stress (kg m^{-2})	Strain %
P_2	5.07	1.17	640
P_3	3.45	1.06	740
P_4	3.27	1.06	920
P_5	2.93	1.05	780

(b) Time of Polymerisation = 2hrs.
Emulsifier concentration varied from 1.25-15%

Sample	Mv x 10^{-5}	Breaking stress (kg m^{-2})	Strain %
P_8	2.32	1.05	720
P_9	2.59	1.07	780
P_{11}	3.58	1.09	780
P_{12}	4.06	1.15	800
P_{13}	4.58	1.16	840

4.3.4. Conclusion.

From the results of the present investigation it is possible to come to a number of conclusions on the emulsion polymerisation of vinyl acetate. These conclusions are

(1) Fatty acid soaps are not good stabilisers for polyvinyl acetate emulsions.

(2) Sodium lauryl sulphate is a better emulsifier than sodium stearate for vinyl acetate emulsion polymerisation.

(3) The generalised theory of emulsion polymerisation applies to the system with some modifications.

(4) In the emulsion polymerisation of vinyl acetate using benzoyl peroxide/ferrous iron couple the control of molecular weight is easier than with water soluble initiators.

(5) The rate of initiation cannot be assumed constant and the molecular weight of the polymer decreases with the time of polymerisation.

(6) The molecular weight is less dependent on emulsifier concentration as stated in the Smith-Ewart theory. For this sysystem

$$\bar{M}v \propto E^{0.24}$$

R E F E R E N C E S

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